

**NOZZLE REFRACTORIES FOR SECONDARY SPECIALTY
STEEL-MAKING VESSELS**

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NOZZLE REFRACTORIES FOR SECONDARY SPECIALTY
STEEL-MAKING VESSELS

by

K.E. Bell* and D.H.H. Quon**

ABSTRACT

Reaction between refractory nozzles for VOD ladles and the ladle contents can lead to nozzle blockage, resulting in lost production. Blockage of the alumina-reinforced mullite nozzles formerly in use at Atlas Steels Company's plant at Tracy, Quebec, is shown to be attributable to growth of a dense zone of products of reaction between refractories and both steel and slag. This paper reports on the reactions between a variety of possible alternative refractory materials, acid and basic, and zircon packing sands, steel and slag that contact the nozzle in service. The ascertained order of resistance to attack is: mullite < alumina < magnesia spinel periclase. Replacement alumina nozzles, indicated by this work, are currently giving satisfactory service.

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INTRODUCTION

Atlas Steels Company, a Canadian specialty steels manufacturer, reported a problem of blockage of the inner nozzles of the vessels used for secondary steelmaking (decarburization, desulphurization, final alloying, etc.) by the Vacuum Oxygen Decarburization (VOD) process. Inasmuch as these vessels also serve as transfer ladles feeding a continuous casting line, even the partial loss of a heat results in serious lost-time penalties, as well as the cost of remelting half a ladle of frozen steel. At the request of the company, work was undertaken in the Mineral Sciences Laboratories of CANMET to investigate the causes of the blockages and to evaluate the suitability of several commercially available alternative nozzle materials. The work was performed under CANMET's Short-Term Assistance in Research and Technology Program (START), Job No. 025180.

A variety of complicating factors rendered it difficult to establish the exact cause, or causes, of blockages:

- The nozzle is comparatively small, hence not a great deal of material is required to reduce metal flow below an acceptable level. When not limited by nozzle size, flow is controlled by a slide-gate directly below the nozzle: a partially closed gate, as used at the beginning of teeming, could induce areas of low metal flow or turbulence in the nozzle that might allow the onset of material build-up, leading to eventual blockage.
- During VOD operations, the nozzle is protected from direct contact with the ladle contents by a filling with zircon sands, a potential source of reaction with the nozzle: on occasion the zircon sinters to form a plug that is burned out with an oxygen lance inserted through the slide-gate.
- Nozzle blockage reached critical proportions with the introduction of production of a heat-resistant, titanium-bearing stainless alloy. Titanium is well-known as an active oxygen getter and for this reason the alloying material is added last, as near as possible to the commencement of teeming, commensurate with adequate mixing time. Nevertheless, titania or titania-corundum type aggregates are known as inclusions in the metal and have been known to reach sufficient size to cause blockage of restricted zones in the casting system. Titanium dioxide would be expected to react aggressively with the aluminosilicate nozzles (1). Other reactive components of the metal would include FeO , Cr_2O_3 and minor manganese.

- Each nozzle is used for at least two or three heats. The end of metal teeming is marked by the appearance of slag in the tundish, when the slide-gate is closed, leaving the nozzle full of slag and exposed to reaction with lime, magnesia, silica and other slag components. After dumping the slag, the nozzle is burned out with an oxygen lance prior to re-use. This procedure could also serve to burn in some of the slag at high temperatures.
- The sequence is then repeated for the succeeding heat.

NOZZLE BLOCKAGE

Post-mortem studies were conducted on fragments of a nozzle blocked or severely restricted after two or three heats. The nozzle was manufactured from an alumina-reinforced mullite based refractory composition, in which three zones could be identified.

First was an apparently unreacted zone, furthest from the nozzle throat. Optical microscopy, confirmed by X-ray diffraction (XRD) analysis, showed this zone to consist of alumina grog in a matrix of mullite. It appeared to be very well burned, if clay bonded, for no cristobalite was detected. In section, it showed a pinkish cast, probably due to iron and titania impurities, which would be expected to be present if the alumina derived from calcined bauxite.

Next toward the nozzle core was an ill-defined grey altered zone. This appears to be the growth zone primarily responsible for nozzle blockage resulting from recrystallization of reaction products arising from the penetration of metal and slag. This zone is dense and strongly intergrown with and adherent to the adjacent original material. It comprises subhedral and anhedral grains of alumina and metal droplets in a complex matrix. A scanning electron micrograph is shown in Fig. 1, along with energy dispersive X-ray (EDXR) maps showing the elemental distribution of Al, Si, Ca, Ti, and Fe. Work by Jenkinson (2) in the high-alumina end of this system has been interpreted by White (3) to indicate that the phases expected here would be corundum, anorthite, calcium titanate and a solid solution of aluminum and iron titanates. The elemental distribution supports the presence of any or all of these phases.

The third zone, which is the central core of the plugged nozzle, is black with white flecks. Optical microscopy, again confirmed by XRD, identified crystalline phases of alumina, rutile, anorthite, monticellite and iron (as metal droplets). The transition from the adjacent reacted zone is again indistinct, with elements of the reacted zone extending into this one, where they appear to be intermingled with a heterogeneous assemblage of phases recrystallized from steel and slag. A section is shown in Fig. 2, along with EDXR maps of the principal elements. The most apparent feature is the white rutile titania, probably recrystallized after dissolution in the slag. This section appears to be silica-poor and the mixed phase assemblage characteristic of the growth zone is dominated here by calcium aluminate rather than anorthite, along with the previously noted titanate phases. What silica is present is largely tied up in the grain boundaries as monticellite (CaMgSiO_4), which would be among the last phases to crystallize on cooling. Chromium is closely associated with the corundum and other aluminous phases, where it is probably substituted in the structure. Analysis by EDXR also indicated some highly complex interstitial phases composed of Al, Ca (or Mg) and Ti along with traces of Fe, Mn and Cr, and also revealed traces of Zr, presumably remnant from the zircon packing sands. Such a heterogeneous phase assemblage most probably represents slag penetration of an almost blocked nozzle, which then cooled under non-equilibrium conditions.

EVALUATION OF ALTERNATIVE MATERIALS

Seven commercially available refractory nozzle materials were examined for their resistance to attack at high temperatures by the zircon sands used for protective packing, by No. 409 stainless steel, and by combined steel and slag. The cup-test method was used, in which blocks of refractory material are core-drilled, the hole is packed with the reactive material and the whole is subjected to high temperature, in this case under high vacuum to more closely simulate conditions in the VOD ladles.

The compositions of the refractories are shown in Table 1. Two types of mullite were examined, one with a conventional sintered bond, the other phosphate bonded. Similarly, two aluminas were evaluated, one ethyl silicate bonded, one phosphate bonded. Basic materials examined comprised

two spinel-magnesia materials, differing in MgO content, and a high-purity periclase material. The microstructure of the two mullites is shown in the scanning electron micrographs of Fig. 3. Both show mullite grains (grog) in an aluminous matrix, however the 'regular' material is dense whereas, with phosphate bonding, the intergranular material is highly porous, probably the result of phosphate loss during firing. Similarly, in Fig. 4, the phosphate bonded alumina shows a well-defined system of large pores, whereas the matrix of the ethyl silicate bonded material, although itself finely porous, shows only a few isolated large pores. Analysis by EDXR showed traces of phosphorous at the boundaries of the large grains and within the smaller grains of the former, and traces of silicon distributed throughout the fine-grained matrix of the latter. The magnesia-spinel materials (Fig. 5) differ principally in the proportions of iron-chrome spinel crystals in a groundmass of fine-grained magnesia-alumina spinel. EDXR showed some calcium in the magnesia spinel and also combined with silicon in many of the grain boundaries. The matrix of the low-magnesia material is significantly more porous than that of the high-magnesia material. The periclase material (Fig. 6) shows tightly bonded periclase grains with only scattered pores at the grain boundaries. The major impurity is iron, with traces of calcium and silicon.

Reaction with Zircon

Two types of zircon sand are used interchangeably to protect the nozzle during the secondary steel-making process. One is a 65 to 100 mesh sand of brown to purple grains when viewed under the microscope. The other is a commercial product, 'Borefil', made up of tan to whitish pellets of 1 to 3 mm diameter, which appear to be sintered zircon aggregates. Only zircon was detectable in either material by XRD.

Cups filled with each material were heated in vacuum at normal teeming temperature (1570°C, 2860°F) for 45 minutes. To determine whether the metal wetted and penetrated the sands, the top quarter of the cup was packed with cuttings of No. 409 stainless steel. After heating, the cups were cut in half and the extent of reaction was examined. Neither sand was penetrated by the molten metal, which formed a button on top.

The results of several cups containing the fine zircon and Borefil packing sands are shown in Fig. 7. There is no indication of other than superficial reaction between the refractories and zircon. Both mullite refractories, particularly the phosphate bonded material, were attacked near the top by the metal. The aluminas and basic materials bore a thin black coating of metals and their oxides, probably vapour transported and showing no perceptible penetration. The zircon sand partially sintered with considerable shrinkage into a still-friable mass: in practice this would expose the upper bore of the nozzle to contact with molten metal, which could be undesirable. The Borefil, however, showed little if any shrinkage and sintering was restricted to points of contact of the grains: the agglomerated mass breaks up readily and seems unlikely to cause any restriction of the nozzle.

The latest phase diagram for $\text{ZrO}_2\text{-SiO}_2$ (4) indicates that zircon dissociates into zirconia and cristobalite at 1676°C ($\approx 3050^\circ\text{F}$) and the first, highly siliceous, liquid phase appears at 1687°C ($\approx 3080^\circ\text{F}$). During the oxygen-blown decarburization process, the exothermic reactions superheat the ladle contents above 1760°C ($\approx 3200^\circ\text{F}$), when temperatures above the dissociation temperature of zircon could conceivably be seen by the zircon-packed nozzle. Hence, the cup tests as above were repeated at 1716°C ($\approx 3120^\circ\text{F}$) for 45 minutes.

The results for the mullite refractories were catastrophic, as shown in Fig. 8, where the reacted residue can be seen inside the broken-away molybdenum safety crucible used to contain all cups and prevent damage to the furnace. Analysis of the reacted mass by XRD showed only mullite and zirconia. Clearly, mullite-based refractories are unsuited to this service as they are completely destroyed by the siliceous liquid phase generated from the zircon at this high temperature.

The extent of attack on the aluminas, spinels, and periclase at this high temperature is shown in Fig. 9 for cups filled with zircon sand with metal on top. It is evident that the silica-rich liquid phase dissolved both classes of alumina, leading to the ultimate recrystallization of mullite. The basic refractories, both spinels and periclase, were similarly attacked, except that the reaction product was forsterite (Mg_2SiO_4). The expected products on cooling dissociated zircon would be cubic and monoclinic zirconia plus cristobalite. No trace of cristobalite was found by XRD analysis, hence the reaction quickly went to essential

completion. The zirconia residue from the fine sand sintered to a very hard, compact billet, which could cause nozzle blockage if it adhered to the wall, or possible blockage of the subsequent slide-gate or assorted shrouds and nozzles.

The Borefil material reacted in an identical manner (Fig. 10) except that the zirconia residue, although showing some shrinkage, retained most of its original texture, offering more protection against the ladle contents, and would be more likely to break up and less likely to cause blockage.

Reaction with Metal

Cups filled with slugs of No. 409 stainless steel, machined to fit snugly in the holes, were heated in vacuum for 45 minutes at each of three temperatures (1543°C, =2810°F; 1570°C, =2860°F; and 1599°C, =2910°F) representing respectively the lower, middle and upper temperatures of normal teeming. Reactions at all temperatures were identical except in degree, and only those at the higher temperature, which showed the greater reaction, are discussed here.

The composition of the steel is: 11.0% chromium, 0.5% manganese, 0.5% silicon, just under 0.2% titanium, and the balance (=87.8%) iron.

Figure 11 shows that the phosphate bonded mullite proved most susceptible to attack. The ethyl silicate bonded alumina was more resistant than its phosphate bonded counterpart. The high-magnesia spinel was more resistant than the low-magnesia material. The periclase, not shown, was the most resistant.

The products of reaction were identical for both mullites. The phosphate bonded material (Fig. 12) suffered greater degradation owing to its higher porosity, shown previously. Note that silicon is absent in most of the grains: the mullite has dissociated with the alumina recrystallizing as lath-shaped corundum with titanium and chromium substituted in the structure; the silica has reacted with iron to form a melt of the approximate composition of Fe_2SiO_4 , which has penetrated the interstitial areas.

An SEM micrograph and EDXR maps are shown in Fig. 13 for phosphate bonded alumina in contact with steel. Reaction with the ethyl silicate bonded material was only superficial, whereas it reached a slightly greater depth in the phosphate bonded material owing to its more-open pore

structure. The reaction products were essentially the same for both aluminas: titanium and chromium substituted in the corundum structure, and iron diffused uniformly throughout except for local concentrations due to inclusions of metal droplets.

The magnesia-spinel refractories also showed good resistance to attack by the metal. Figure 14 shows the reacted zone of the low-magnesia material, which (as expected) showed greater depth of penetration due to its more-open original porosity. It is difficult to judge the extent of reaction with chromium and iron as both are major constituents of the refractories. An attempt was made to establish quantitatively the penetration of titanium, but only trace amounts could be detected by EDXR analysis.

The periclase material has the highest resistance to attack by molten metal, as evidenced by the very thin reacted zone of Figure 15. Some metal penetration along grain boundaries has occurred at the interface, otherwise the microstructure is identical to that of the unused material.

Reactions with Slag/Metal

The seven alternative refractory materials were examined by cup-test against attack by a mixture of 50-50 wt % of No. 409 stainless steel cuttings and final slag from a typical VOD heat (Table 2). It should be noted that slag compositions vary considerably during the process, some being in the range where calcium disilicate phases might be expected to crystallize. The cups were again tested at three temperatures over the normal teeming temperature range and again only the results for the higher temperature, 1559°C (=2910°F), are presented.

The sectional test cups are shown in Figure 16, from which it is evident that the order of resistance to combined slag and metal is: mullite < alumina < magnesia-spinel < periclase. The phosphate bonded materials were less resistant than their equivalents with alternative bonding. The trend in the basic refractories is toward increasing resistance with increasing magnesia.

In both mullites (Fig. 17) the reacted zone shows the growth of randomly oriented, lath-shaped crystals mainly at the interface. The interstices contain either a glassy phase or anhedral fine-grained materials; cristobalite and anorthite were identified by XRD. An SEM micrograph of the growth zone in the regular mullite material is shown in

Fig. 18 and EDXR analyses of the various phases in this zone are given in Table 3. The lath-shaped crystals are mainly alumina and the matrix is glass and/or anhedral crystals of calcium-alumina-silica composition. Evidently the mullite in contact with slag/metal dissociated, the alumina mostly recrystallized from the melt, and the silica partly recrystallized as cristobalite and partly reacted with calcium and alumina in the melt, which glassified and partially devitrified on cooling. Interestingly, plant trials using phosphate bonded material gave better results - less blocking - than the regular bonded mullite, which is contrary to the indications from the cup tests. However, the more-porous phosphate bonded material would contain more intercrystalline liquid at high temperatures, rendering it more likely to erode rather than block during teeming.

Again, the reacted zone is wider in the phosphate bonded alumina than in the ethyl silicate bonded material (Fig. 19) owing to the more-open porosity of the phosphate bonded material. The products of reaction, identified by XRD, are the same in both cases: anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and gehlenite ($2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) are present as lath-like crystals and as reaction rims surrounding alumina crystals in what is considered a growth zone. Scanning electron micrographs of the ethyl silicate bonded alumina after contact with metal/slag at 1599°C ($\approx 2910^\circ\text{F}$) are shown in Fig. 20, and the EDXR analyses of the phases present are given in Table 3. At the interface (top) alumina has recrystallized in prismatic form, with the interstices filled with calcium-aluminum silicates. The metals carried in the slag, principally titania and chrome, are primarily substituted in the structure of the recrystallized alumina. Slightly behind the interface (bottom) the slag has penetrated the grain boundaries of the polycrystalline alumina and rounding indicates partial dissolution of the grains. Some recrystallized alumina is present, but in this relatively alumina-poor environment most of the metals remain with the calcium-alumina-silica materials filling the interstices.

The spinels (Fig. 21) show only a narrow reacted zone, with considerably less slag penetration than the aluminas. Monticellite (CaMgSiO_4) and both alpha- and beta-dicalcium silicate were identified as reaction products at the surface and in the residual slag. Scanning electron micrographs of the low-magnesia spinel are shown in Fig. 22, and EDXR analyses of the various phases present are given in Table 3. The major phases detected in the reaction zone are periclase, and solid

solutions of Cr, Al, Fe and Mg spinel, presumed to be essentially original components of the refractory materials. Unquestionably the grains closest to the surface have been modified (by counter diffusion with the metal/slag), witness the presence of CaO , TiO_2 and MnO , none of which are recorded in the chemical analysis of the original material: the extent of exchange of Cr, Mg and Al cannot be gauged as they are originally present in both the refractory material and the metal/slag. Notable is the lack of SiO_2 in any of the areas analysed by EDXR, even though the analysis of the original material reported 2.7% SiO_2 . The evidence suggests that SiO_2 is largely excluded from penetration of the refractory material, remaining in the slag to form monticellite and dicalcium silicates on cooling.

The periclase material (Fig. 23) shows little change from the original texture except for a thin dense face where the slag has dissolved some magnesia, which has recrystallized as forsterite (Mg_2SiO_4). Beta-dicalcium silicate was also identified in the residual slag by XRD. Figure 24 is an SEM micrograph of the slag/metal-periclase interface, and quantitative chemical analyses of the phases in this zone are given in Table 3. Partial dissolution of the periclase grains is evident from the rounded grains nearest the surface, surrounded by slag. The slag penetrates along the grain boundaries (cf. point B). Diffusion of chrome into the periclase grains is evident, where it has formed internal blebs of chrome-magnesia spinel to produce a structure reminiscent of that of fused-grain chrome-magnesia refractories. This should be an advantage, as this structure is more resistant than periclase to attack by siliceous slags. Minor alumina and titania appear to have accompanied the chrome and to be substituted in the spinel lattice.

On cooling to room temperature, the residual slag in the basic cups usually decrepitated to a fine powder, attributed to the dicalcium silicate component. On cooling from high temperature, dicalcium silicate undergoes a series of polymorphic inversions accompanied by volume changes that stress the material to the point where it decrepitates (5). This could be advantageous as it would negate the need to burn out the nozzle between heats. However, it seems likely that re-using the ladle while it is still hot would be preferable on grounds of energy efficiency.

SUMMARY

The blockage of alumina-reinforced mullite nozzles has been shown to be attributable to the growth of a dense zone of products of reaction between refractories and metal/slag. Mullite is not a suitable replacement material, and its use above the dissociation temperature of zircon would be catastrophic. Alumina is acceptably resistant to attack and has been subsequently proven in plant operations: a dense ethyl silicate bonded material is preferred, as the porosity resulting from phosphate bonding allows more penetration by the reactive materials. Basic materials, both magnesia-spinel and periclase are resistant to attack by both metal and slag. A potential advantage of their use is that the unreacted slag is self-decrepitating. However, care should be exercised to use only dense materials as penetration of significant amounts of slag could lead to decrepitation of the refractories along with the slag.

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REFERENCES

1. White, J. "Igne non frangor - An assessment of recent research on refractories (Part Two)"; Refract J 52:Jan.-Feb.; 1977.
2. Jenkinson, D.A., M.Sc. Tech. Thesis, Sheffield University; 1972.
3. White, J. "The chemistry of high-alumina bauxite-based refractories with special reference to the effects of TiO_2 - A review"; Trans J Br Ceram Soc 81:109-111; 1982.
4. In Phase Diagrams for Ceramists, 1969 Supplement, E.M. Levin, C.R. Robbins and H.F. McMurdie, Eds., The American Ceramic Society, Inc., Pub.; 1969.
5. Muan, A. and Osborn, E.F. "Phase equilibria among oxides in steelmaking"; Addison-Wesley Publishing Company, Reading, Mass.; 1964.

Table 1. Chemical compositions of the refractories

	MES	MPB	Refractories*		Z500	Z700	MAG
			AT2D	HIAPB			
Al ₂ O ₃	70.0	71.2	96.0	97.6	33.0	21.1	—
SiO ₂	27.5	24.4	3.5	—	2.7	3.5	—
Fe ₃ O ₄	—	—	—	—	5.6	—	—
Fe ₂ O ₃	0.8	0.8	—	—	0.2	3.0	—
TiO ₂	1.6	1.6	—	—	—	—	—
MgO	—	1.9	—	1.9	49.0	62.1	99.0
Cr ₂ O ₃	—	—	—	—	1.0	1.0	—
Alkalies	—	—	—	—	1.0	1.0	—
Others	0.1	0.1	0.5	0.5	—	—	—

*MES = Regular mullite, MPB = Phosphate-bonded mullite, AT2D = Ethyl silicate-bonded alumina, HIAPB = Phosphate-bonded alumina, Z500 = Spinel, Z700 = spinel, MAG = Magnesia.

Table 2. Typical composition of the slag

CaO	52.0%
MgO	11.0
MnO	0.2
FeO	1.0
Al ₂ O ₃	2.5
Cr ₂ O ₃	1.2
SiO ₂	31.3
SO ₂	0.3
Ti	0.5

Table 3. Chemical composition of the phases at the metal/slag refractories interface, by quantitative EDXR

Refractory Type	Location Analysed	Al ₂ O ₃	SiO ₂	CaO	Oxide, % TiO ₂	Cr ₂ O ₃	MnO	FeO	MgO
Regular Mullite (Fig. 18)	lath	93.95	0.20	0.10	0.36	5.26	—	0.13	—
	matrix	26.67	44.86	18.85	4.28	3.24	0.17	1.93	—
Alumina, Ethyl Silicate (Fig. 20)	A lath	82.81	2.22	10.42	2.50	1.99	0.01	0.06	—
	B interstice	23.85	33.61	41.80	0.46	0.14	0.13	—	—
	C grain	99.54	0.10	—	0.11	0.09	—	0.09	—
	D interstice	26.72	41.11	28.77	3.16	0.10	0.02	0.12	—
Spinel, low Mg (Fig. 22)	A Cr/Fe sp	12.38	—	—	0.84	55.03	0.18	12.52	19.05
	B Cr/Al sp	50.05	—	0.38	0.34	24.02	—	0.80	24.41
	variant	53.11	—	0.47	0.29	20.62	—	0.74	24.77
	C Cr/Al sp	72.63	—	1.12	1.03	13.15	0.69	1.15	10.15
	D Cr/Fe sp	14.55	—	0.15	0.81	53.10	—	15.96	15.44
	E reacted	63.70	—	8.90	0.62	0.10	—	1.65	25.10
	F periclase	7.03	—	—	2.38	0.26	0.10	4.50	85.70
	G rim	67.84	—	0.11	0.45	1.71	0.04	3.45	26.91
Magnesia (Fig. 24)	A original	0.12	0.38	0.83	0.26	2.18	0.02	1.17	95.00
	B pore	0.43	34.16	61.83	0.76	—	—	—	2.82
	C dark bleb	2.85	0.30	0.59	1.52	51.36	—	0.48	42.91
	C matrix	0.22	0.30	0.23	0.10	7.45	—	1.10	90.60
	D interstice	1.07	32.12	55.77	0.54	0.47	—	0.16	8.84

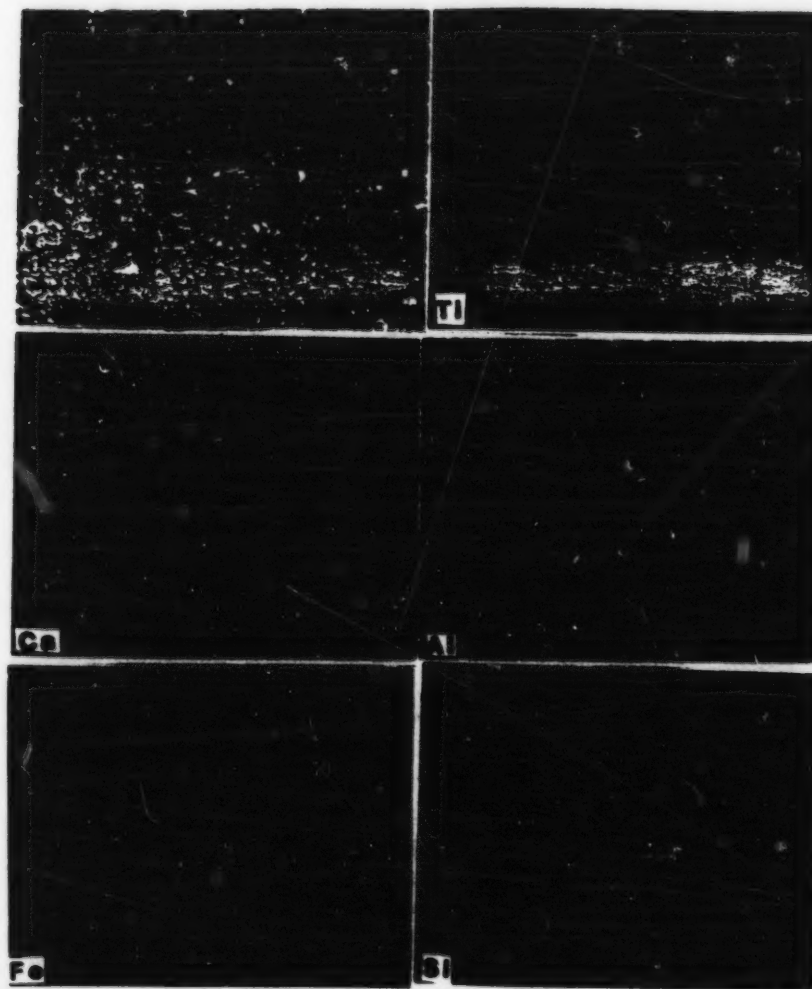


Fig. 1 - SEM micrograph of altered (growth) zone of blocked nozzle,
with EDXR maps showing elemental distribution.

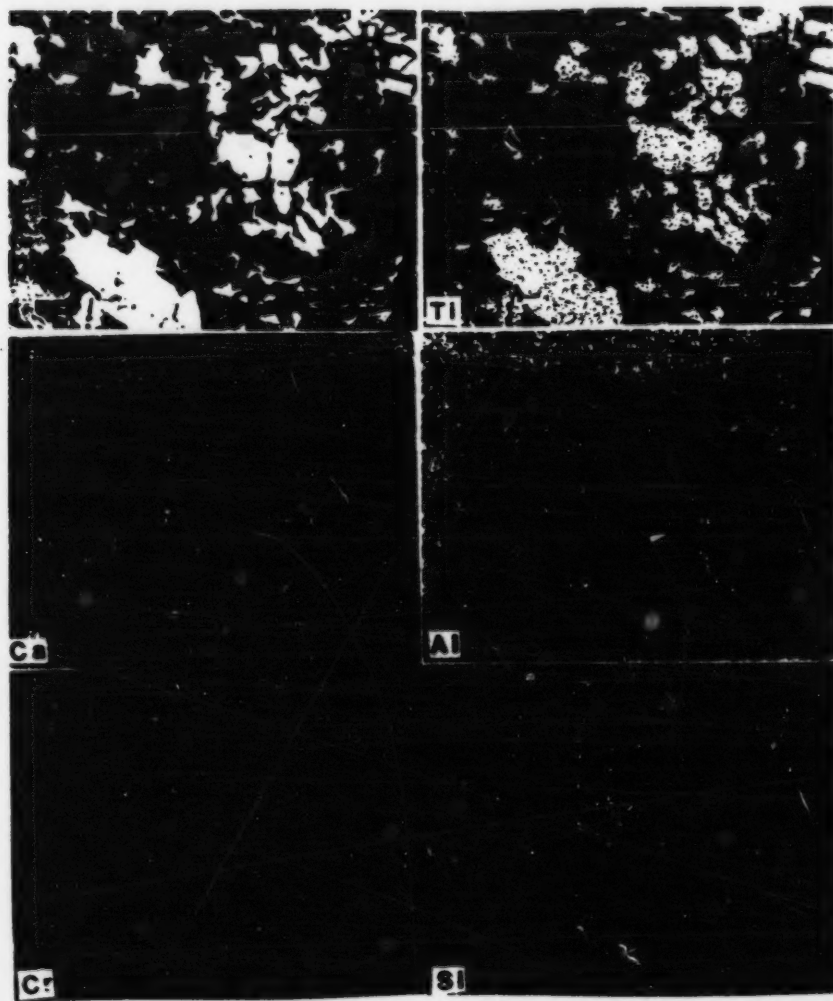


Fig. 2 - SEM micrograph of slagged core of blocked nozzle, with EDXR maps of elemental distribution.

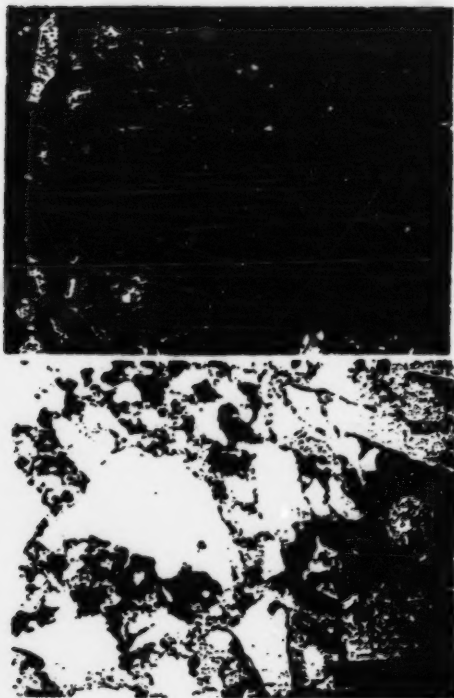


Fig. 3 - Microstructures of
mullite refractories;
top; regular bond,
bottom; phosphate bond.

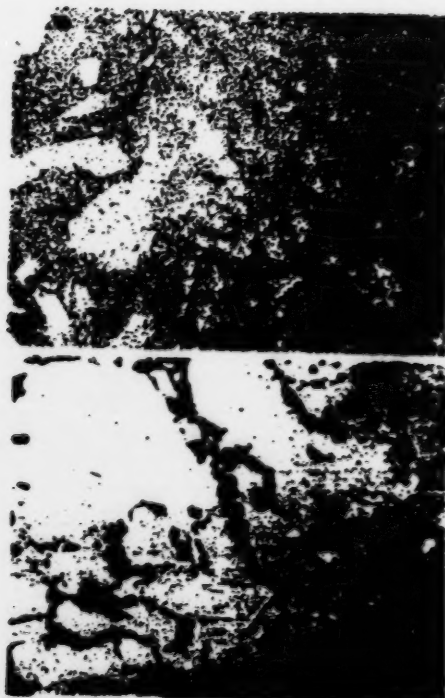


Fig. 4 - Microstructures of
alumina refractories;
top; ethyl silicate bond,
bottom; phosphate bond.

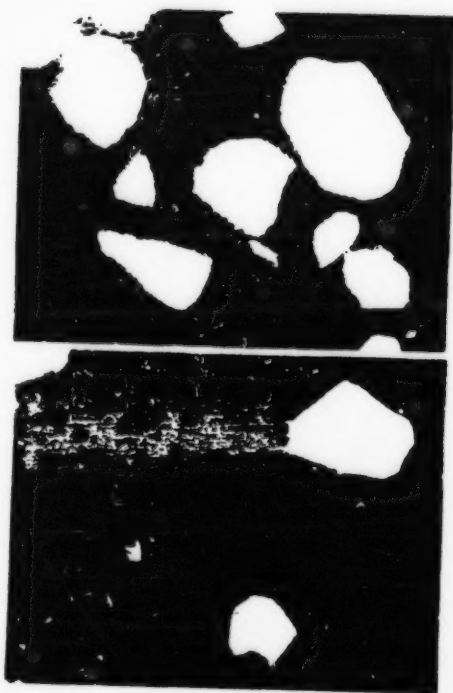


Fig. 5 - Microstructures of
magnesia-spinel
refractories:
top; low magnesia,
bottom; high magnesia.

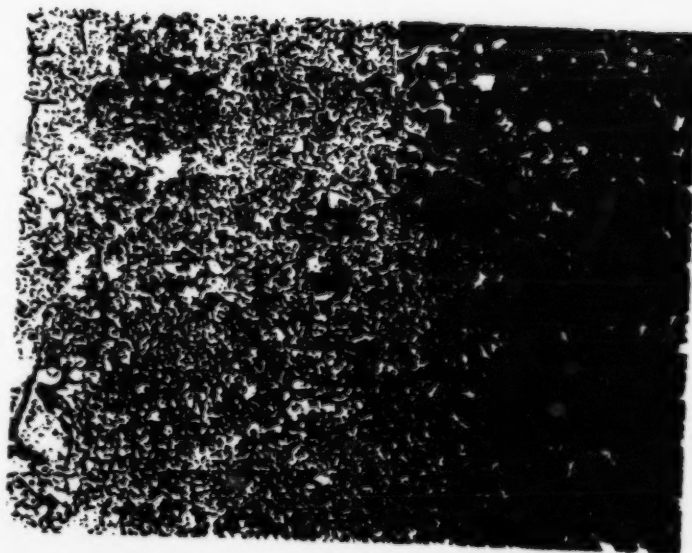


Fig. 6 - Microstructure of periclase refractory material.

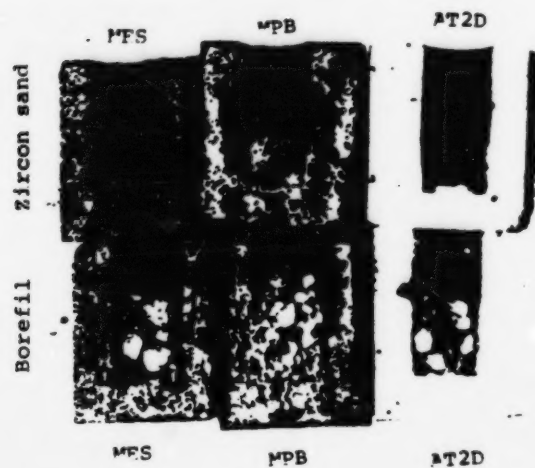


Fig. 7 - Cup tests with zircon packing sands under metal, 1570°C (2860°F) for 45 minutes.

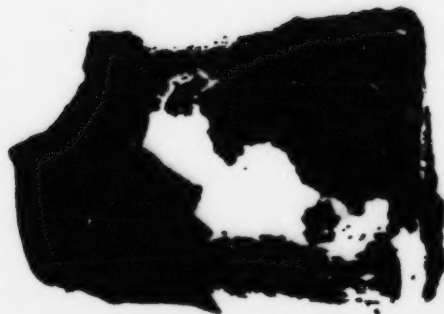


Fig. 8 - Phosphate bonded mullite cup reacted with zircon sand and metal at 1716°C (3120°F) for 45 minutes.



Fig. 9 - Alumina, magnesia-spinel and periclase cups reacted with zircon sand and metal at 1716°C (3120°F) for 45 minutes.



Fig. 10 - Alumina, magnesia-spinel and periclase cups reacted with Borefil and metal at 1716°C (3120°F) for 45 minutes.

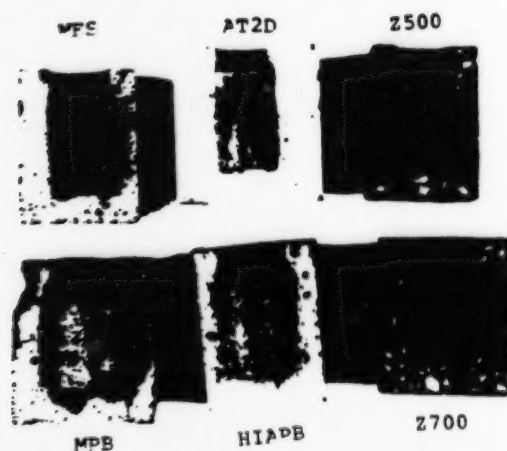


Fig. 11 - Cup tests with No. 409 stainless steel: 1599°C ($\approx 2910^{\circ}\text{F}$) for 45 minutes.

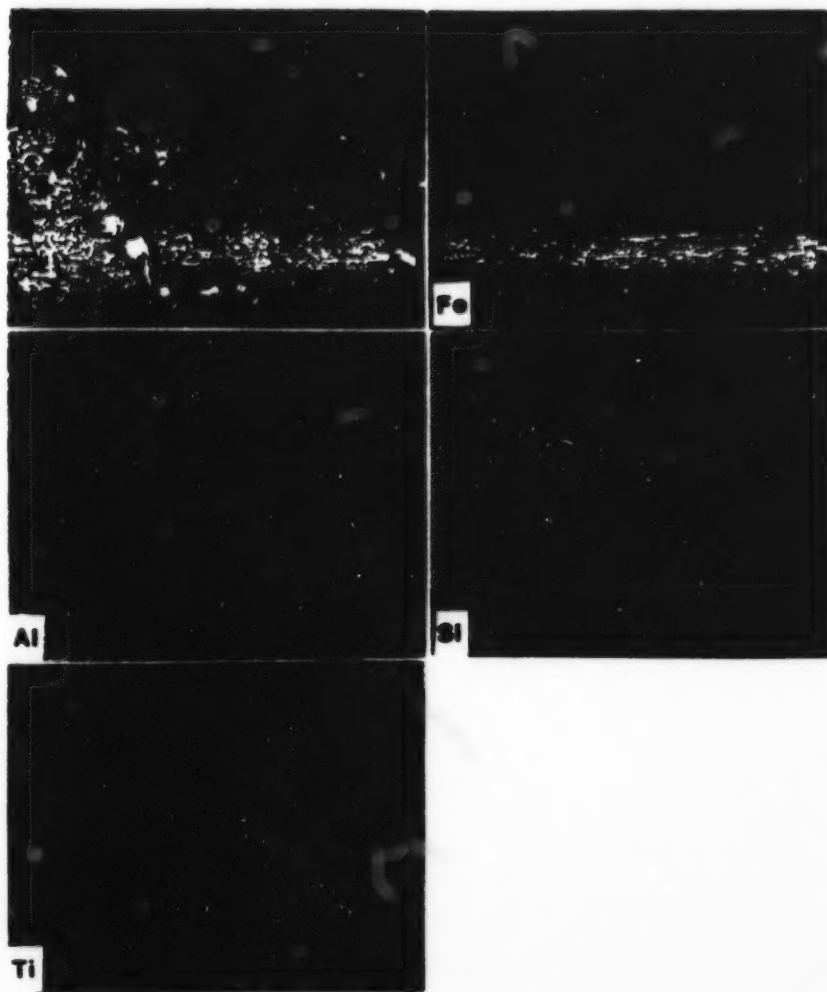


Fig. 12 - Section of reacted zone of phosphate bonded mullite in contact with steel at 1599°C ($\sim 2910^{\circ}\text{F}$) for 45 minutes, with EDXR maps showing elemental distribution.

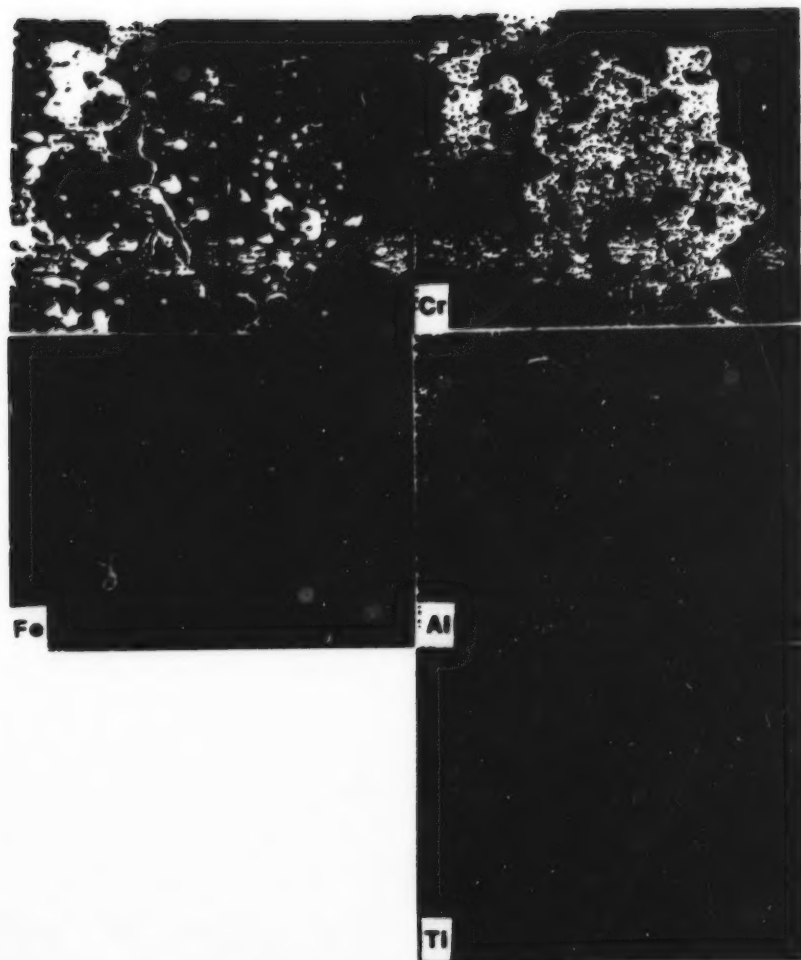


Fig. 13 - Microstructure and elemental distribution of phosphate bonded alumina reacted with steel at 1599°C ($\sim 2910^{\circ}\text{F}$) for 45 minutes.

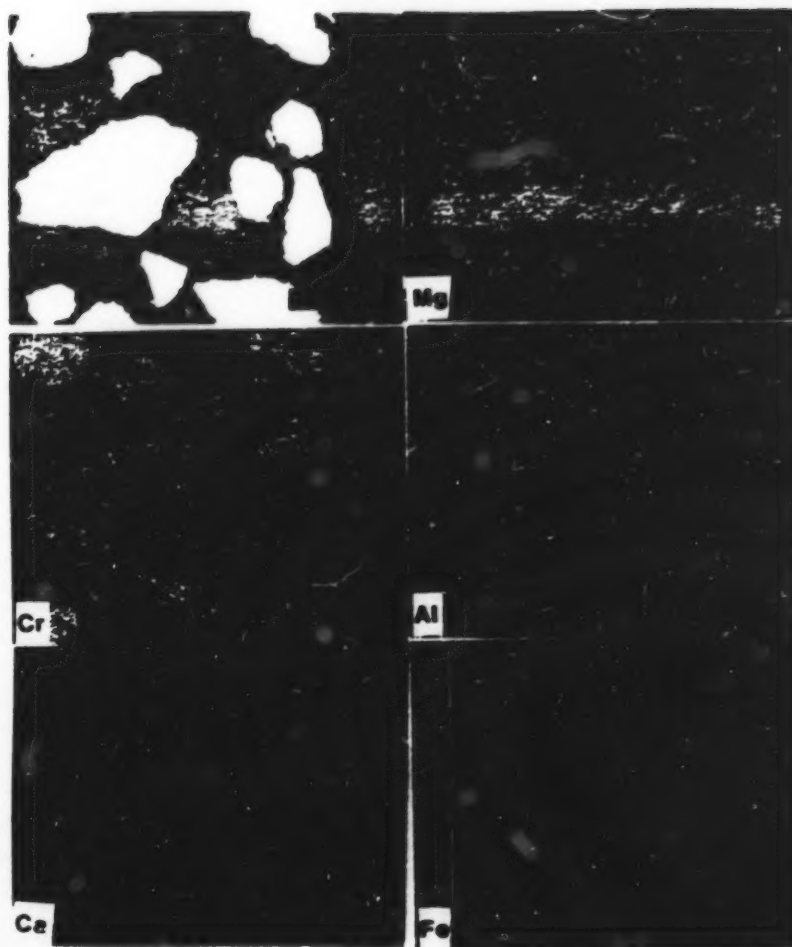


Fig. 14 - Microstructure of reacted zone of magnesia-spinel material (Z500) contacted by metal at 1599°C (~2910°F) for 45 minutes.

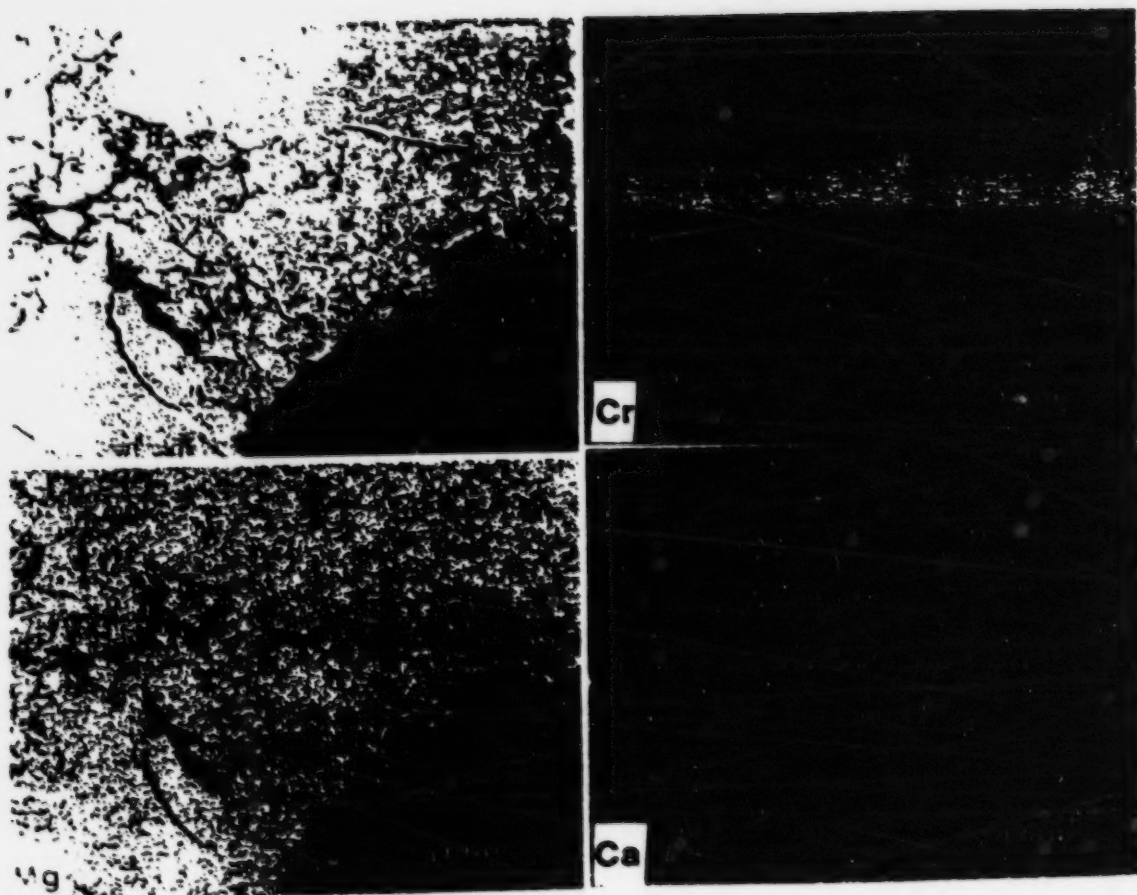


Fig. 15 - Microstructure of periclase-metal interface after heating to 1599°C ($\approx 2910^{\circ}\text{F}$) for 45 minutes.

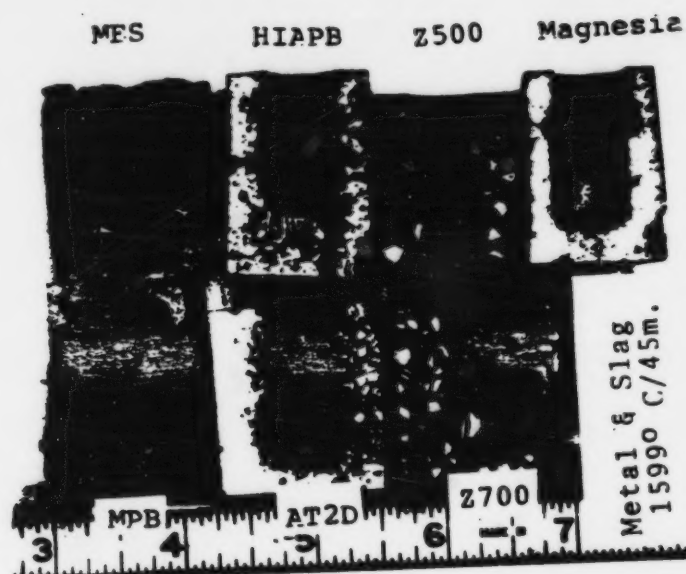


Fig. 16 - Cup tests with 50-50 wt% metal and slag, 1599°C (~2910°F) for 45 minutes.

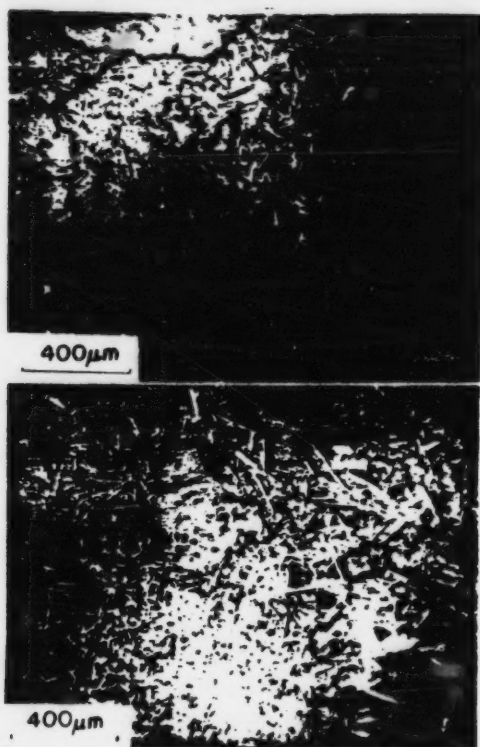


Fig. 17 - Photomicrographs of the mullites reacted with metal and slag at 1599°C ($\sim 2910^{\circ}\text{F}$) for 45 minutes:

top; regular bond,
bottom; phosphate bond.

Fig. 18 - SEM micrograph of growth zone of regular mullite reacted with metal and slag at 1599°C ($\sim 2910^{\circ}\text{F}$) for 45 minutes, $\times 400$.



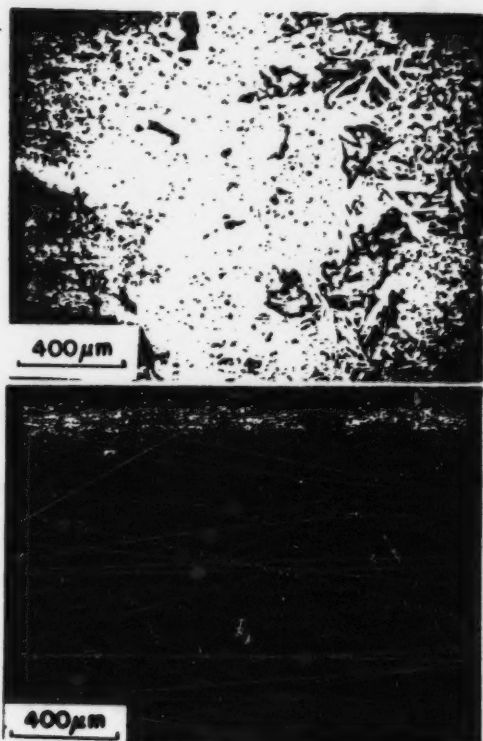


Fig. 19 - Photomicrographs of the aluminas reacted with metal and slag at 1599°C ($\sim 2910^{\circ}\text{F}$) for 45 minutes:

top; ethyl silicate bond,
bottom; phosphate bond.

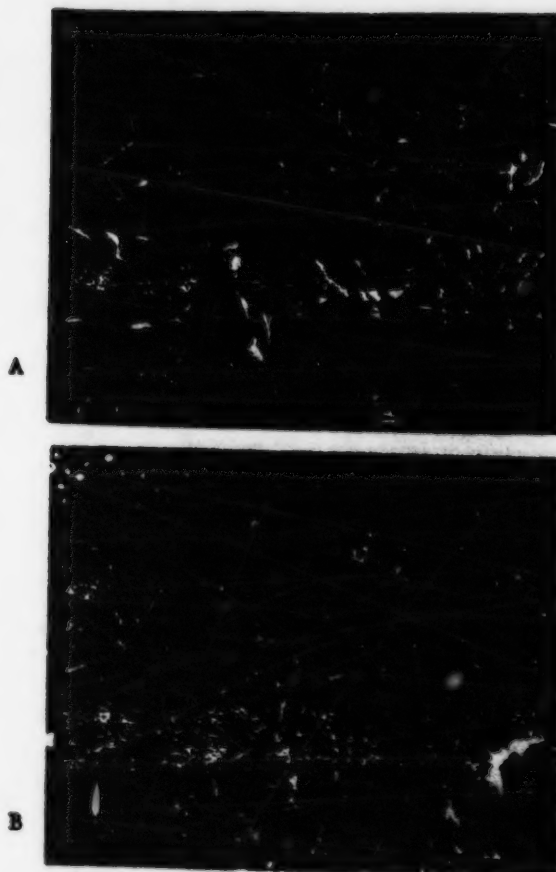


Fig. 20 - SEM micrograph of ethyl silicate bonded alumina reacted with metal and slag at 1599°C ($\sim 2910^{\circ}\text{F}$) for 45 minutes:

A; fully reacted zone, x 800,
B; penetrated zone, x 400.

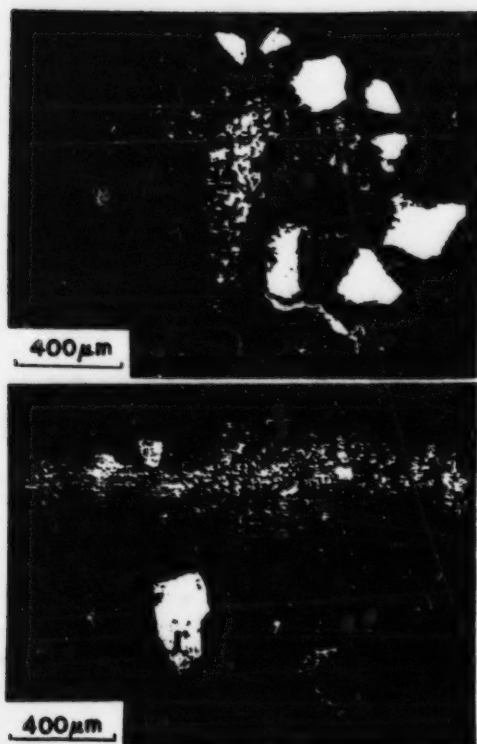
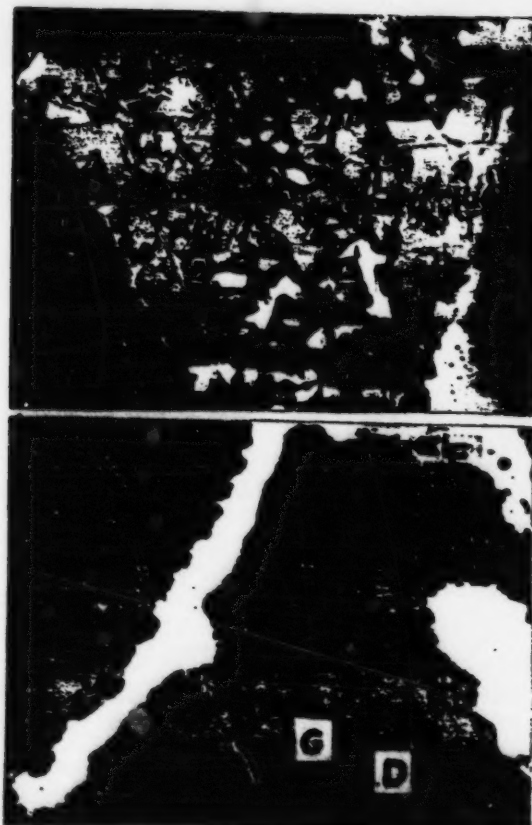


Fig. 21 - Reaction of magnesia-spinel refractories with metal and slag at 1599°C (~2910°F) for 45 minutes:

top; low magnesia,
bottom; high magnesia.

Fig. 22 - SEM micrograph of low magnesia spinel reacted with metal and slag at 1599°C (~2910°F) for 45 minutes:

top; x 400,
bottom; x 100.



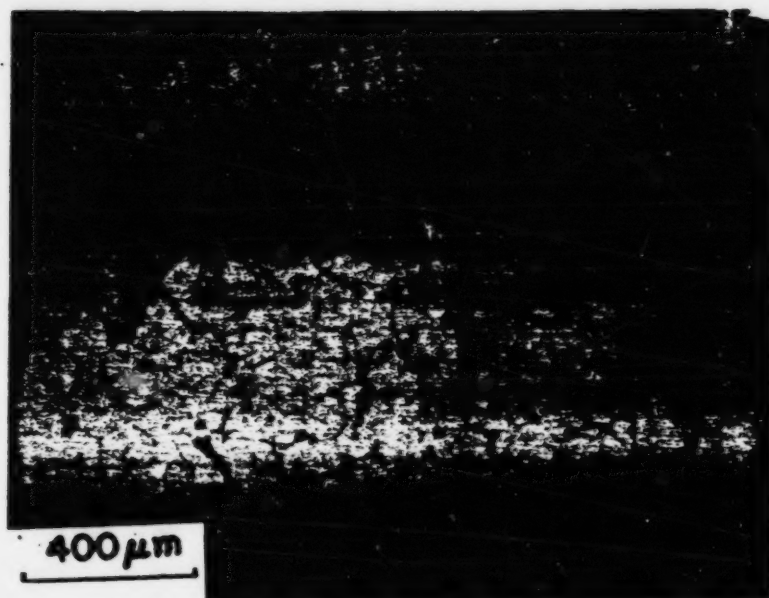


Fig. 23 - Interface between periclase refractory material and slag/metal, reacted at 1599°C (~2910°F) for 45 minutes; x 62.5.

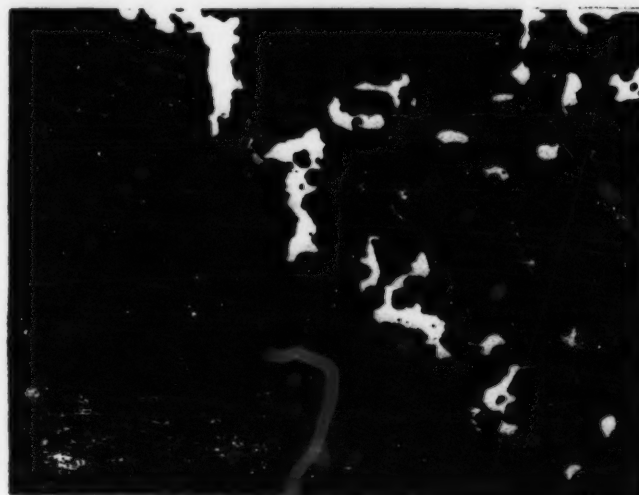


Fig. 24 - SEM micrograph of periclase material reacted with metal/slag at 1599°C (~2910°F) for 45 minutes; x 200.